Isoprene Rubber Filled with Silica Generated *In Situ*

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ABSTRACT: We modified synthetic isoprene rubber by means of the *in situ* generation of silica particles through the sol–gel process starting from tetraethoxysilane (TEOS) as an inorganic oxide precursor. Different reaction conditions were investigated with variations in the initial TEOS content, the reaction time of the sol–gel process, and the presence of a coupling/surfactant agent (octyltriethoxysilane). Organic–inorganic hybrid materials with a silica content up to 70 phr were obtained with the complete conversion of TEOS to silica for a long enough sol–gel reaction time. A very homogeneous dispersion of silica particles was observed in all cases together with a very good adhesion between the filler and matrix. The size of the *in situ* generated silica was controlled by the appropriate addition of octyltriethoxysilane. Swelling and extraction tests and dynamic mechanical analysis indicated that the vulcanization process of isoprene rubber was perturbed by the sol–gel process; this led to a slight decrease in the crosslinking degree. However, a significant reinforcing effect due to the presence of silica particles was observed for all of the investigated samples. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3422–3428, 2011

**Key words:** elastomers; fillers; nanoparticle; rubber; silicas

INTRODUCTION

In addition to carbon black, which is one of the most used reinforcing fillers for rubber materials (especially in the tire industry), particulate silica represents the one of the most important filler used for reinforced elastomeric composites. Silica compounding offers several advantages over that of carbon black, such as whiteness, excellent tear strength, abrasion resistance, and heat buildup reduction. One of the main drawbacks in the use of silica prepared by the conventional precipitation methods is the high extent of agglomeration of the inorganic particles within the rubber matrix due the strong filler–filler interactions, which can result in high compound viscosity and, thus, difficult mixing and processing. Furthermore, the incompatibility between silica and elastomers, such as styrene–butadiene rubber or natural rubber (NR), which leads to poor filler–rubber interaction, often requires the use of silane coupling agents to improve the reinforcing efficiency of silica.

An alternative and interesting approach to the incorporation of preformed particulate fillers within the rubber matrix by mechanical mixing (compounding) before its vulcanization (*ex situ* process) is the *in situ* generation of inorganic oxides (silica but also titania, alumina, zirconia, etc.) by means of the sol–gel process, according to a bottom-up approach to obtain organic–inorganic hybrid materials.

The sol–gel process involves the generation of ceramic-type materials by the hydrolysis and condensation reactions of organometallic compounds such as metal alkoxides. One of the most important reaction of this type is the hydrolysis and condensation of tetraethoxysilane (TEOS) to form silica according to the following reaction:

$$Si(OCH_2CH_3)_4 + 2H_2O \rightarrow SiO_2 + 4CH_3CH_2OH \quad (1)$$
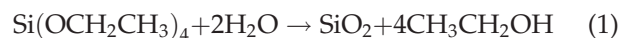
Organic–inorganic hybrid materials can be prepared with these reactions in the presence of organic molecules or macromolecules, which should preferably contain functional groups to improve their bonding to the inorganic phase.

The possibility of preparing elastomers modified with metal oxides generated *in situ* by the sol–gel process has been already reviewed in several publications.[1–7]

The preparation of butadiene rubber,[8] acrylonitrile–butadiene rubber,[9,10] NR, and styrene–butadiene rubber[11,12] modified with *in situ* generated silica has been reported, and nanometer-size silica particles up to about 80 phr were generated via a

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sol–gel reaction of TEOS. Ikeda and coworkers[8–12] investigated the effect of different amines, and the polarity and solubility in water of amine were found to be influential factors for controlling the silica content and morphology in the rubbery matrix.

The functional triblock copolymer polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polystyrene (SEBS) was modified and reinforced with TEOS; 3-glycidyloxypropyl trimethoxysilane was used as a coupling agent. The tensile strength of the hybrids showed a considerable improvement over that of pure SEBS together with an increased interfacial interaction between the organic and inorganic phases.[13] In a similar way, flexible hybrid materials were synthesized by the incorporation and reaction of tetrabutyl titanate and TEOS within amino-functionalized SEBS.[14]

Thermoplastic polyurethane elastomer/silica hybrids were prepared with a modified sol–gel process. The storage modulus (G') increased because of the reinforcement of the *in situ* silica. The tear strength decreased significantly with increasing *in situ* silica content.[15,16]

Metallocene poly(ethylene octene) elastomer (POE), acrylic acid grafted metallocene poly(ethylene octene) elastomer (POE-*g*-AA), and maleic anhydride grafted poly(ethylene octene) elastomer (POE-*g*-MAH) were modified with TEOS, silicic acid, and a tetra isopropyl orthotitanate ceramic precursor to obtain silica- or titania-based organic–inorganic hybrids. The authors reported that the POE-*g*-AA (POE-*g*-MAH)/SiO$_2$ (or TiO$_2$) hybrids enhanced the properties of the POE/SiO$_2$ (or TiO$_2$) hybrid because the interfacial forces of the former were the covalent Si—O—C (Ti—O—C) and hetero-associated hydrogen bonds, but the latter only had weaker hydrogen bonds. Mechanical and thermal analysis showed that both the tensile strength and the glass-transition temperature (T_g) increased to a maximum value and then decreased with increasing SiO$_2$ or TiO$_2$.[17–21]

Silicone resins filled with various silica particles prepared from TEOS and vinyltriethoxysilane were investigated before and after crosslinking. Once the matrix was crosslinked, the tensile strength and the elongation at break decreased. A further significant increase in the mechanical properties was obtained in the case of good adhesion between the matrix and silica particles from vinyltriethoxysilane.[22]

A specific method was developed for the preparation of polydimethylsiloxane nanocomposites with unusually high transparency by means of the *in situ* generation of silica, zirconia, and titania particles by a two-step sol–gel procedure in which the required water of hydrolysis was simply absorbed from the air, and the catalyst was generated *in situ* from a tin salt. Electron microscopy showed that the silica domains were well dispersed and very small (30–50 nm). Stress–strain measurements indicated that the particles provided very good reinforcement.[23,24]

To the best of our knowledge, to date, the effect of the generation of silica particles into a *cis*-1,4-polyisoprene matrix has been investigated only on NR, whereas no attention has been paid to isoprene rubber (IR), the synthetic NR counterpart. Although NR consists almost exclusively of *cis*-1,4-isoprene units and contains a small portion of nonrubber components, IR has a lower content of *cis*-1,4-isoprene units but a greater purity. Compared with NR, IR is somewhat inferior in mechanical strength, antiaging properties, and crystallization, but it is superior in the consistency of product, uniformity of cure rate, and processability, so it is especially well suited for injection-molded compounds.

We recently presented a study on the *in situ* generation of silica from TEOS into IR and its influence on the material dynamic mechanical behavior.[25] The *in situ* generated silica particles were homogeneously dispersed in the vulcanized rubber with dimensions of a few nanometers to the submicrometer scale. In the presence of a coupling agent [bis(3-triethoxysilylpropyl) tetrasulfide], a good polymer–filler adhesion was observed. The dynamic mechanical behavior was nonlinear for silica contents higher than 20 wt %. In this range of compositions, silica exerted a remarkable reinforcement on the low-amplitude G', which was related to the silica content according to the Huber–Vilgis model.[26] One of the main drawbacks of the used synthetic procedure concerned the fact that the water necessary for the hydrolysis and condensation reactions of TEOS to silica was simply absorbed from the humid external environment without any strict control of the stoichiometry. As a result of the restricted diffusion of water from the environment to the reactive mixture, the conversion of TEOS to silica was limited to samples having a high initial content of TEOS.

To overcome this problem, in this article, we present a further investigation on the synthesis and the resulting morphology of IR/silica organic–inorganic hybrids prepared with better control of the stoichiometry.

EXPERIMENTAL

Materials

TEOS, octyltriethoxysilane (OTES), dibutyltin dilaurate, dicumyl peroxide, ethanol (EtOH), and toluene were purchased from Sigma–Aldrich (Milan, Italy) and were used without further purification.

Synthetic *cis*-1,4-polisoprene (i.e., IR; Sigma–Aldrich) had a 97% content of *cis* units, a viscosity-

average molecular mass of 2.3×10^6 g/mol, a T_g of $-67°C$, and a density of 0.91 g/cm^3.

Preparation

IR polymer (4 g) was dissolved in toluene (100 mL) at the refluxing temperature, and after it was cooled at room temperature, given amounts of TEOS, H_2O, and EtOH (TEOS : H_2O : EtOH = 1 : 4 : 4 mol), dibutyltin dilaurate (2 wt % relative to TEOS, as a catalyst for the sol process), and dicumyl peroxide (1 wt % relative to IR, as a vulcanizing agent) were added.

In some case, OTES (4 wt % relative to IR) was added at different reaction times as a surfactant during the silica particle growth. The mixture usually assumed the aspect of an emulsion with the presence of a significant amount of water in an organic medium taken into account. The mixture was magnetically stirred and heated at 80°C for different times (from 0.5 to 15 h) to activate the hydrolytic condensation of TEOS to silica. After a given reaction time, toluene and other volatile products, such as H_2O and EtOH, were eliminated with a rotary evaporator operating at a reduced pressure and room temperature to prevent any significant further progress of the sol–gel reaction.

All of the samples were molded into disks (diameter = 100 mm, thickness = 1.5 mm) and cured at 150°C for 20 min under a pressure of 150 bar with a hot-plate hydraulic press (Carver, Ltd. Wabash, IN).

The prepared materials were coded as IR/SiO$_2$ x_y, where x represents the nominal final SiO$_2$ content (phr) calculated by stoichiometry under the assumption of the complete conversion of TEOS to silica and y represents the reaction time (min) of the sol–gel reaction. For formulations containing OTES, the prepared materials were coded as IR/SiO$_2$ $x\_y\_OTES(z)$, where z represents the time at which OTES was added to the reacting system.

Characterization

Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 429 CD apparatus (Selb/Bavaria, Germany) to measure the actual silica content. A sample (20 mg) was placed in a platinum pan and heated under air up to 800°C at a heating rate of 20°C/min.

The swelling experiments were run by the immersion of samples with a size of $1.5 \times 3 \times 7$ mm^3 into toluene at room temperature for several days. Toluene was replaced daily with fresh solvent to eliminate all uncrosslinked fractions, such as unvulcanized IR chains, which would lead to wrong values of the swelling ratio. When the swollen mass (m_s) reached a constant value, the sample was dried to a constant mass [i.e., the dried mass (m_d)], and the

absolute swelling ratio (q) was evaluated from an average of at least three measurements according to the following equation:

$$q = \frac{m_s}{m_d} \qquad (2)$$

The absolute extractable fraction (f) was determined as follows:

$$f = \frac{m_0 - m_d}{m_0} \times 100 \qquad (3)$$

where m_0 is the mass of the sample before its immersion in toluene.

q and f were also related to the actual IR content (i.e., the swellable phase and, in the case of incomplete vulcanization, the extractable phase), and these values were called q_{IR} and f_{IR}, respectively. Their values were calculated as follows:

$$q_{IR} = \frac{q}{C_{IR}} \qquad (4)$$

$$f_{IR} = \frac{f}{C_{IR}} \qquad (5)$$

where C_{IR} is the weight fraction of IR present in the composite.

The morphological investigation was carried out with scanning electron microscopy (SEM; Quanta 200, FEI, Eindhoven, The Netherlands) by the application of an accelerating voltage of 15 kV. The sample surfaces (cross section) were coated with gold by an electrodeposition method to impart electrical conduction before the SEM micrographs were recorded.

Dynamic mechanical tests were performed with a DMTA IV apparatus (Rheometric Scientific, Reichelsheim, Germany). The tests were run in shear sandwich mode on circular specimens (diameter = 7 mm, thickness = 1.5 mm), and the specimens were heated at 3°C/min from -80 to 25°C at a frequency of 1 Hz and at a shear strain of 0.025%. Multiple-frequency tests were also run in the frequency range 1–30 Hz.

RESULTS AND DISCUSSION

Kinetic analysis

We followed the progress of the sol–gel reaction by determining the real silica content through TGA at different reaction times. The real silica content values were reported as a function of the reaction time, as shown in Figure 1, for the IR/SiO$_2$ x_y and IR/SiO$_2$ 30$\_y\_OTES(0)$ samples.

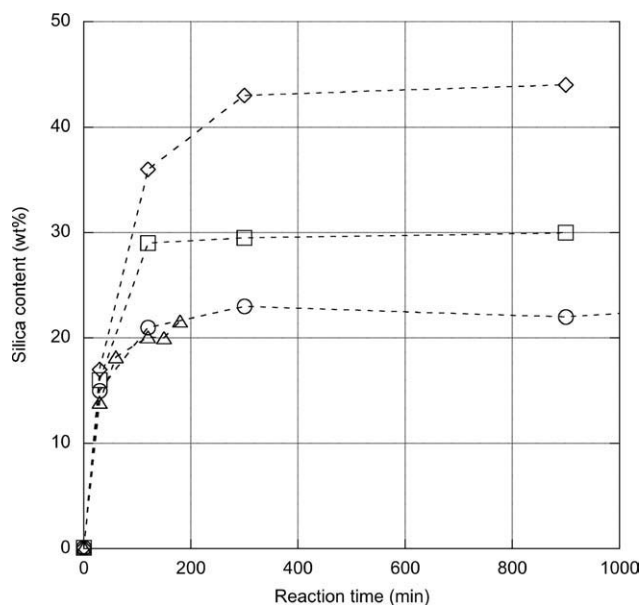The maximum silica weight percentages (i.e., by assumption of the complete conversion of TEOS to

Figure 1 Silica content (determined by TGA) as a function of the reaction time for ($\bigcirc$) IR/SiO$_2$ 30_y, ($\square$) IR/SiO$_2$ 50_y, ($\diamond$) IR/SiO$_2$ 70_y, and ($\triangle$) IR/SiO$_2$ 30_y_OTES(0).

SiO$_2$) for the IR/SiO$_2$ 30_y, IR/SiO$_2$ 50_y, and IR/SiO$_2$ 70_y samples were 23.1, 33.3, and 41.2 wt %, respectively. The data reported in Figure 1 indicated that silica content values very close to the maximum were obtained for all of the samples after a reaction time in the range 200–300 min.

The data clearly indicated that the introduction of the correct amount of water in the reactive mixture (contrary to what was obtained with the previously reported[25] synthetic procedure) gave an almost quantitative conversion of TEOS to silica for long enough reaction times.

Also, the addition of OTES in the initial formulation did not affect the kinetics of the sol–gel reaction, as indicated by the data concerning IR/SiO$_2$ 30_y_OTES(0), which substantially overlapped to those of IR/SiO$_2$ 30_y for similar reaction times.

Extraction and swelling tests

The values of q, q_{IR}, f, and f_{IR} in toluene are reported in Table I.

With the fact that conversion of TEOS to silica was almost quantitative for the samples reported in Table I, as indicated by TGA, the extractable fraction in toluene was mainly derived from the uncrosslinked fraction of IR. In other words, it could be considered an indicator of the progress of the vulcanization reaction of IR.

For the unfilled elastomer IR, the swelling value was a direct indication of the crosslinking degree obtained after vulcanization. In the case of the filled elastomers, the swelling behavior could have been

the result of complex and different phenomena, such as the crosslinking degree of the rubber matrix, which could have been influenced by the sol–gel reaction; the toluene absorption contribution of the silica phase; the ability of the silica particles to act as crosslinking points; and so on. The values of q_{IR} (i.e., the swelling ratios referring only to the organic rubber phase) indicated a linear increase with the increasing silica content attributable to the decreasing crosslinking density of the rubber phase after vulcanization. This hypothesis was also supported by the observation that f_{IR} in toluene increased with increasing silica content (and, thus, the initial TEOS concentration); this clearly indicated an interfering effect of the sol–gel reaction of TEOS to silica with respect to the vulcanization process of the rubber.

From swelling and extraction tests, it was possible to conclude that the *in situ* generation of silica particles by means of the sol–gel process led to a hindering effect on the vulcanization process, which limited the extent of the crosslinking of the IR phase.

Morphology

SEM micrographs of the cross sections for the IR/SiO$_2$ x_y and IR/SiO$_2$ 30_y_OTES(z) samples are presented in Figures 2–4.

The development of the morphology of 30 phr IR/SiO$_2$ as a function of the sol–gel reaction time is reported in Figure 2. Spherical silica particles with an average diameter of about 1 μm were observed after 30 min of reaction together with some aggregates of larger size. The average diameter of the dispersed particles increased to 1.5–2 μm after 120 min, and the presence of agglomerates was significantly reduced. No significant changes in the morphology were observed with prolonged reaction times up to 900 min. A very homogeneous dispersion of silica particles within the IR matrix was observed in all cases, together with a very good adhesion between the filler and matrix, as evidenced by the absence of any voids at the interface.

According to this SEM analysis, the development of the silica morphology (particle shape and size) seemed to occur in the early stages of the reaction (reaction time = 30 min), and no significant changes

TABLE I
Swelling Ratios (q and q_{IR}) and Extractable Fractions (f and f_{IR}) of the IR and IR/SiO$_2$ x_y Samples

Sample	q (w/w)	q_{IR} (w/w)	f (%)	f_{IR} (%)
IR	4.5	4.5	6.0	6.0
IR/SiO$_2$ 30_180	3.9	5.1	5.2	6.8
IR/SiO$_2$ 50_180	3.6	5.4	5.4	8.1
IR/SiO$_2$ 70_180	3.9	6.7	9.0	15.3
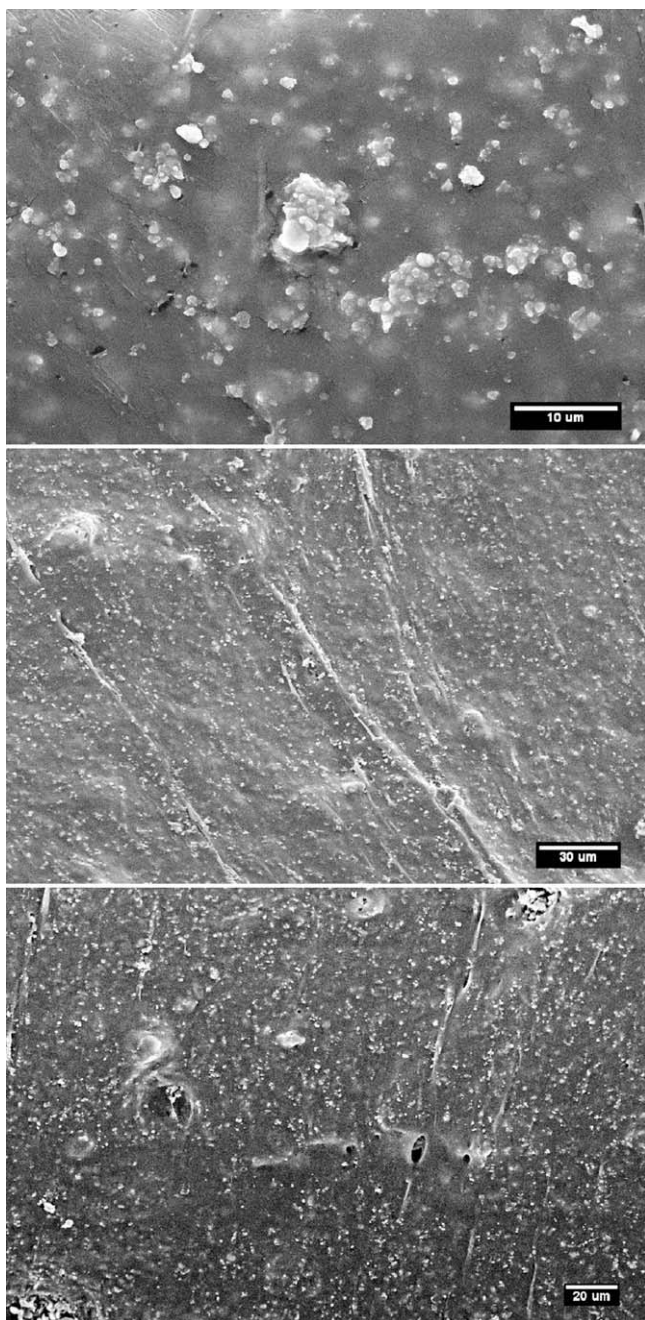
Figure 2 SEM micrographs (cross sections) of IR/SiO$_2$ 30_30 (top), IR/SiO$_2$ 30_120 (middle), and IR/SiO$_2$ 30_900 (bottom).

The micrographs reported in Figure 3 (and compared to those of Figure 2) seemed to indicate that no significant effect on the size and distribution of silica particles was obtained with the addition of OTES to the reactive mixture from the beginning of the reaction. We speculated that the triethoxysilane groups of OTES, when added from the beginning, reacted with TEOS in the early stages of the reaction and octyl groups, remaining entrapped in the bulk of the forming inorganic silica network, did not explicate their action as a surfactant/coupling agent at the surface of the silica particles.

On the contrary, when OTES was added after 30 min to the reacting mixture, that is, after the nucleation and partial growth of the silica particles, a reduction in the average size of the dispersed phase was noted (see Fig. 4). On the basis of this analysis, the addition of OTES after a partial conversion of TEOS (that is, after the nucleation of the silica particles) seemed to stabilize the surface of the growing particles and to reduce their average dimensions, and the OTES seemed to act as an effective surfactant agent.
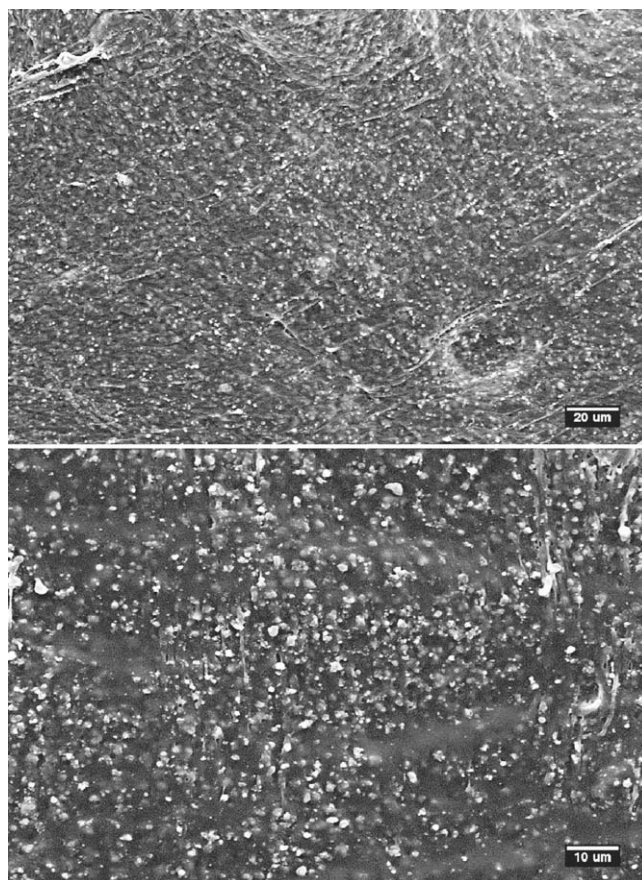
in particles size and distribution were observed after 120 min of reaction.

The presence of triethoxysilane groups and octyl groups in the OTES molecules should have ensured both the reactivity toward the inorganic phase during the silica particle growth and the interaction with the organic IR matrix. To verify its effectiveness as a coupling agent and/or surfactant and, thus, the effect on the final morphology of the hybrids, OTES was added to the reaction mixture at different times (sol–gel reaction times = 0 and 30 min, respectively).

Figure 3 SEM micrographs (cross sections) of IR/SiO$_2$ 30_30_OTES(0) (top) and IR/SiO$_2$ 30_150_OTES(0) (bottom).
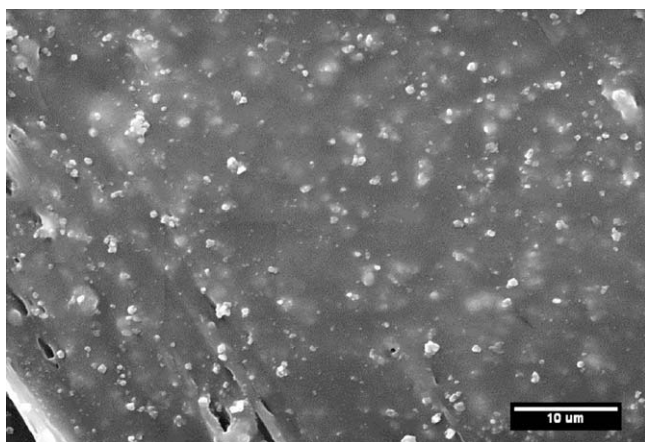
Figure 4 SEM micrograph (cross section) of IR/SiO$_2$ 30_150_OTES(30).

Figure 5 Multiple-frequency test data: the natural logarithm of the frequency (ln f) versus the reciprocal of T_g for ($\bigcirc$) IR and ($\square$) IR/SiO$_2$ 70_120.

Dynamic mechanical analysis

The T_g and G' values measured below and above T_g for the unfilled IR and IR/SiO$_2$ x_120 samples obtained by dynamic mechanical thermal analysis are reported in Table II.

Quite surprisingly, T_g (measured from both the tan δ peak and inflection point of the G' curve) decreased with increasing content of silica. Contrary to what was expected, the presence of silica particles tended to increase the flexibility of the composite materials. This unexpected behavior was, however, in agreement with the swelling and extraction, which indirectly showed a decrease in the crosslinking density of the vulcanized rubber because of the interfering effect of the sol–gel reaction during the vulcanization process.

A further explanation of this small tendency to a decreased T_g for nanofilled polymers with respect to the pristine matrix was derived from the experimental observation reported for thermoplastics modified with carbon nanotubes, nano-ZnO, and nano-Al$_2$O$_3$,[27–29] for which researchers have suggested a

higher mobility of polymer chains due to the higher free volumes caused by the presence of nonadhering nanoobjects inside the polymer bulk.

The G' data above T_g indicated a significant reinforcing effect due to the presence of silica particles. G' measured at 0°C of IR/SiO$_2$ x_120 samples was 2.5–3.6 times higher than the value corresponding to unfilled IR. The G' values measured at 0°C did not exhibit a monotone trend with increasing silica content, but a maximum value for the IR/SiO$_2$ 50_120 sample was observed. The G' values of the filled elastomers in the rubbery plateau depended on both the crosslinking degree of the rubber matrix and the content of the rigid dispersed phase. For the investigated samples, the presence of a maximum value of G' for intermediate silica content (50 phr) could have presumably been the result of two different contributions, that is, the increasing filler content and the decreasing crosslinking density, as indicated by swelling and extraction experiments.

The apparent activation energy for glass transition (ΔE_a) was used to characterize the relationship between the shift of T_g and the frequency. ΔE_a was determined with the Arrhenius relationship and by the plot of the natural logarithm of the frequency against the reciprocal of T_g given by the chosen peak maxima; this gives a straight line from which ΔE_a can be obtained as the product of the slope and the value of the universal gas constant (8.314 cal mol^{-1} K^{-1}). The multiple-frequency data of the IR and IR/SiO$_2$ 70_120 samples are reported in Figure 5.

The ΔE_a values calculated on the basis of Figure 5 were 138 kJ/mol for IR and 157 kJ/mol for IR/SiO$_2$ 70_120, respectively. As a reference, a value of about 146 kJ/mol was determined by means of differential scanning calorimetry measurements and was reported for polyisoprene.[30]

As expected, the calculated ΔE_a values indicated that the presence of a rigid silica phase within the

TABLE II
Dynamic Mechanical Analysis Results (T_g and G') of the IR and IR/SiO$_2$ x_120 Samples

Sample	T_g (°C)[a]	T_g (°C)[b]	G' (MPa)	
			$T < T_g$[c]	$T > T_g$[d]
IR	−42	−46	42	0.33
IR/SiO$_2$ 30_120	−43	−49	34	0.82
IR/SiO$_2$ 50_120	−46	−51	35	1.20
IR/SiO$_2$ 70_120	−47	−55	36	1.10

T = temperature.
[a] Measured from the tan δ peak.
[b] Measured from the inflection point of the G' curve.
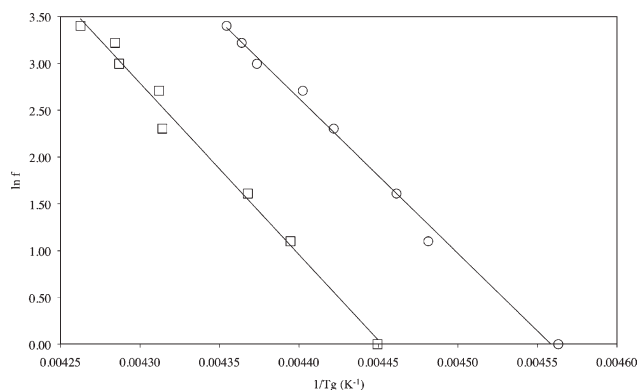[c] Measured at −60°C.
[d] Measured at 0°C.

rubber matrix led to a hindering effect of the glass-transition process with an increase in ΔE_a of approximately 15% with respect to the unfilled rubber.

CONCLUSIONS

The proposed synthetic procedure was an effective method for the *in situ* generation of reinforcing silica within the IR matrix. For a long enough reaction time, the sol–gel process led to a quantitative conversion of the TEOS precursor to silica with the obtainment of a homogeneous distribution of spherically shaped particles. The delayed addition of OTES as a coupling/surfactant agent was effective for controlling the average size and the aggregation phenomena of the *in situ* generated silica. Dynamic mechanical analysis carried out on the filled IR showed a significant reinforcement (in terms of G' increments) with respect to the pristine elastomer. On the other hand, both swelling and extraction tests suggested that the sol–gel process perturbed the vulcanization process of IR; this led to a slight decrease in the crosslinking degree of the rubber matrix.

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